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NEW NONLINEAR OPTICAL FILM PROCESSING

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This program concerned improving the linear optical properties (i.e., transparency) of ordered polymers. These materials have demonstrated high values of $\chi^{(3)}$ but are not useful for NLO applications because their poor optical quality restricts their use as optical waveguides. Optical quality is defined as transparency and surface flatness, the specific goals of which are reduction in optical loss to less than 1 dB/cm and a reduction in the surface roughness to an optically flat surface of less than 1/4 wavelength. Our approach to introducing these desired improvements in film quality has been to modify the film processing conditions.

This program has examined many of the process steps involved in the fabrication of ordered polymer films to determine their effect on the film's optical quality, hence, nonlinear optical performance. Initial efforts focused on poly p-phenylene benzobisthiazole (PBZT), as this is the most technically advanced ordered polymer and it is with this particular ordered polymer Foster-Miller has had its most extensive film processing experience. More recent efforts have involved poly p-phenylene benzobisoxazole (PBO).

Over the course of the program, the optical loss, alpha, decreased from 1064 to about 660 cm^{-1}. While significant, these losses are still prohibitive for NLO materials. Our processing changes have also led to 3-fold modulus improvements and nearly 60 percent strength improvements, to 13.9 GPa and 157 MPa, respectively, in biaxial PBO film.

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1. EXECUTIVE SUMMARY

This program concerned improving the linear optical properties (i.e., transparency) of ordered polymers. These materials have demonstrated high values of $\chi^{(3)}$ but are not useful for NLO applications because their poor optical quality restricts their use as optical waveguides. Optical quality is defined as transparency and surface flatness, the specific goals of which are reduction in optical loss to less than 1 dB/cm and a reduction in the surface roughness to an optically flat surface of less than 1/4 wavelength. Our approach to introducing these desired improvements in film quality has been to modify the film processing conditions.

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Figure 2 reveals the improvements in optical loss made over the course of the 3-year program. While these improvements are not sufficient as to render PBZ's useful for nonlinear optical applications, the modifications in the process steps have resulted in film with improved mechanical properties (Figure 3).

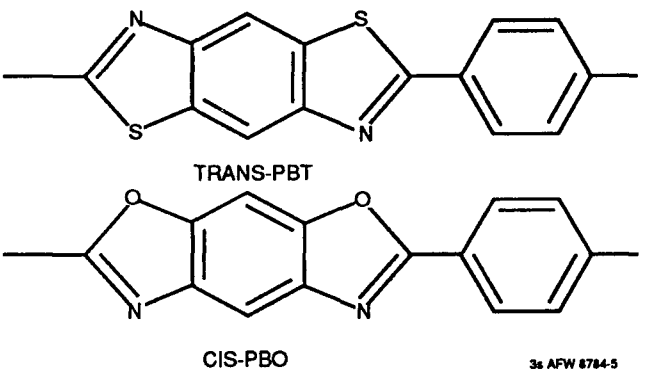


Figure 1. Structure of Ordered Polymers Processed

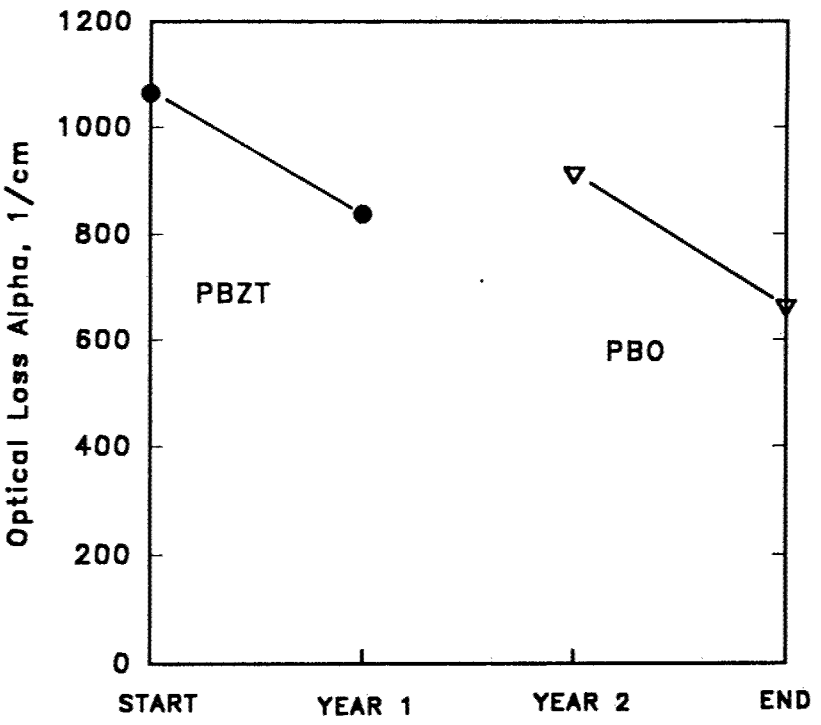


Figure 2. Improvement of Optical Quality of the Film During the Program

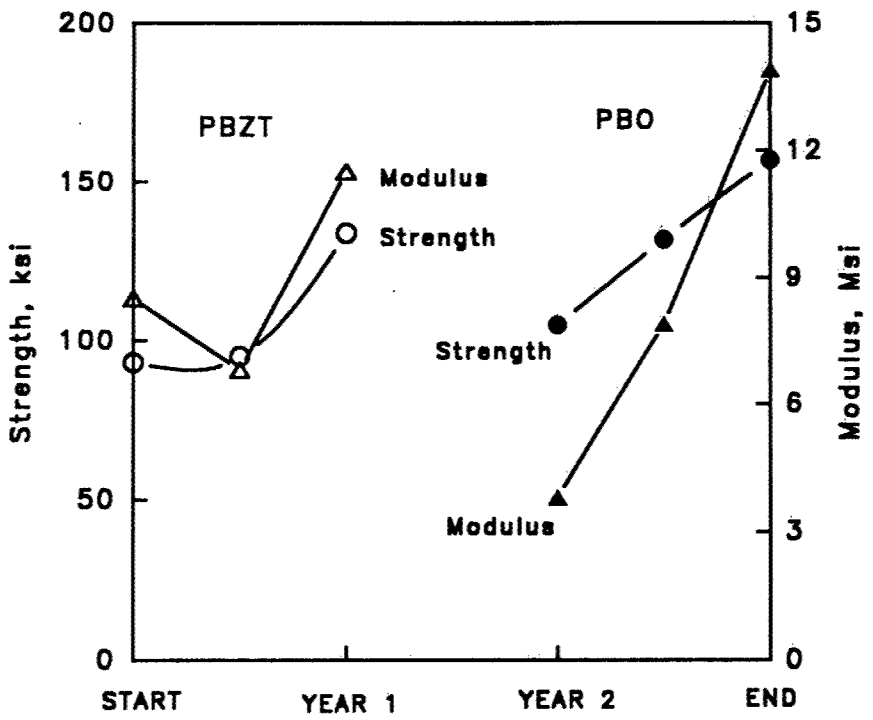


Figure 3. Improvement of Mechanical Properties of Film (0.2 mil, ±22.5 deg, MD) During the Program

During the first year we focused on the Tasks 1 to 4 outlined in the program schedule in Figure 4. Our approach was to analyze each component of the existing film production methods and correlate its relationship with the film properties. We also experimented with different approaches to film extrusion and solution processing in order to improve the optical quality of the films. Our efforts in that period included the development of experimental methods to measure optical quality of films to provide rapid feedback on the success of each of the approaches.

In summary, the major accomplishments of the first year were:

- The relationship between polymer solution filtration and void content in films was demonstrated

- The relationship between polymer solution homogenization and film clarity and physical properties was defined

- A new processing system for film extrusion was designed; component procurement of this system was initiated.

As a result of these experiments, we concluded that the necessary steps to properly treat the polymer solution should involve the following:

- Filter the polymer solution
- Homogenize (mix) the solution
- Degas the solution.

The system designed to accomplish these three tasks is shown schematically in Figure 5. It consisted of a co-rotating twin screw extruder through which the polymer solution (dope) is passed. After the extruder, the polymer is passed sequentially through a gear pump and a fine filter of 5 or 10 μm pore size, and finally through a spinneret die and into an evacuated collection pot.

In the second year of this program, our efforts focused on two specific areas. The first of these was the improvement of the film processing and extrusion system designed in the first year. This effort included the setup and testing of the twin screw extruder. This system has been used for the enhanced homogenization, degassing, and filtering the PBZ dopes. The second area of focus was the study of the PBZ film coagulation process. The goal of this effort was to better understand the effect of modification of the coagulation process on the morphology of the polymer

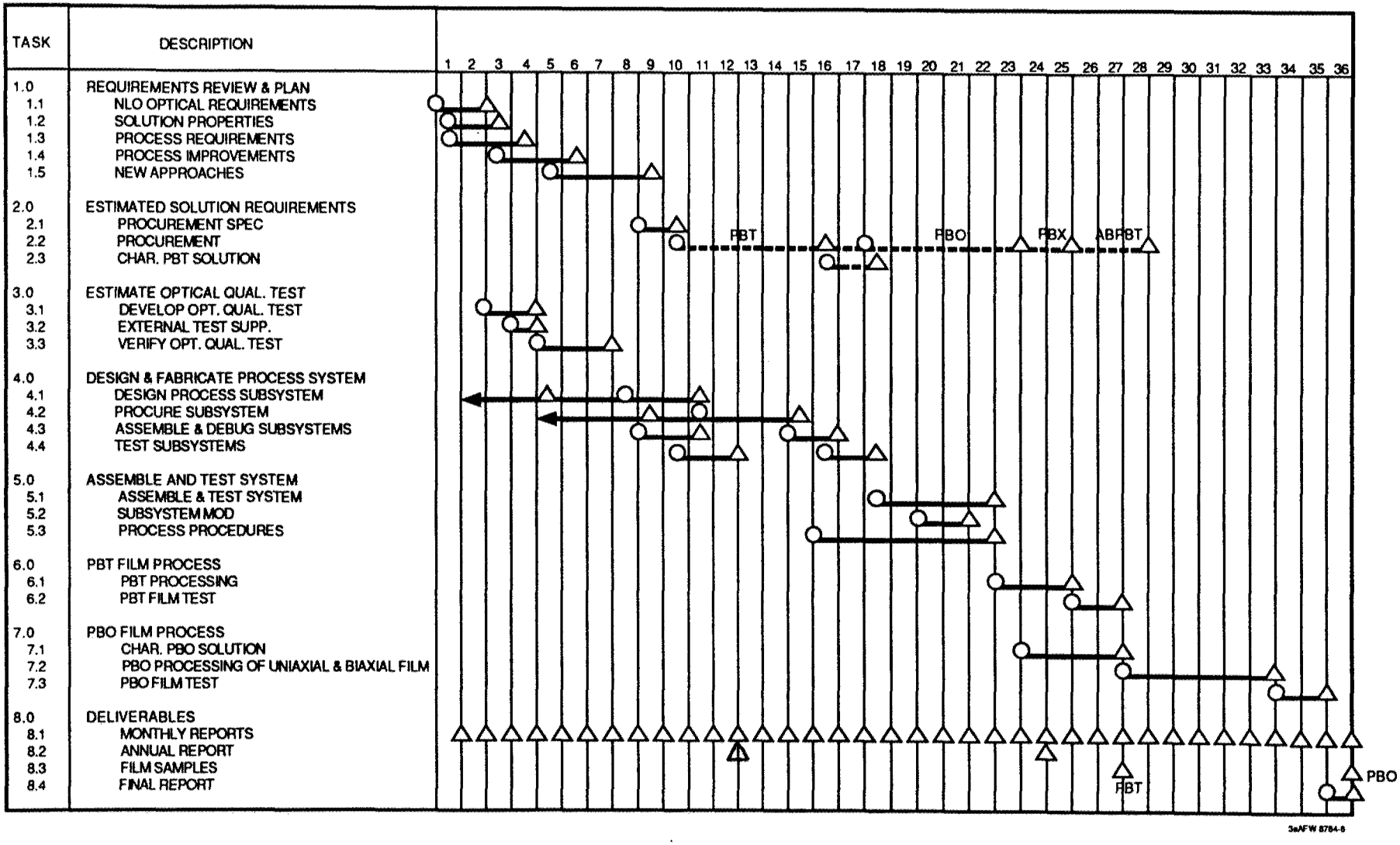


Figure 4. Program Schedule

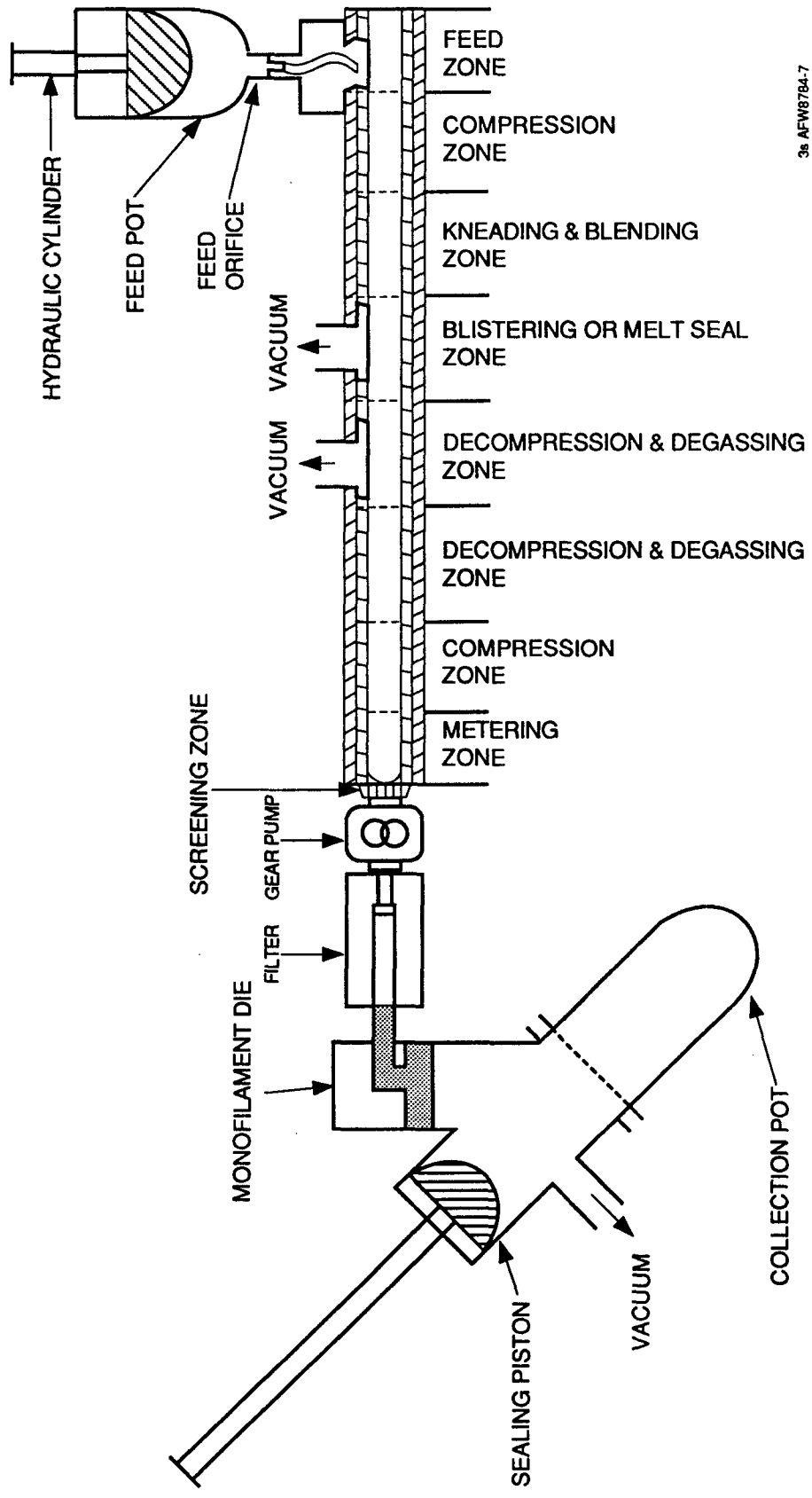


Figure 5. Berstorff Twin Screw Extruder Setup

films. In this way we hoped to enhance the optical quality of these films. These efforts of the second year correspond to Tasks 5 and 6, shown in Figure 4. In addition to these two primary areas of focus, we also designed, fabricated, and constructed a high pressure filtration cell for the improved filtration of the PBZ polymer solutions and dopes. This new filtration cell had the capability of using submicron pore size filters.

In summary, the focal points of the second year effort were:

- To set up and test the new twin screw (Berstorff 40 mm diam 35/1 L/D (ZE40)) process system

- To examine an alternative method of film processing (hand-cast low viscosity solutions of highly filtered PBZT or PBO) in the event that the new process system did not produce film of suitable optical quality

- To fabricate a high pressure, batch filtration device for the production of highly filtered (<1μ) PBZT dopes and solution.

While the twin screw extruder and the corresponding improvements in the filtration, homogenization, and extrusion of the PBZ dope brought about a significant reduction in the void content and increased the homogeneity of the biaxial PBZ films, only a slight improvement in optical quality was evident with respect to films that were processed without this system, as were shown in Figure 2.

The hand-cast PBZ film study accomplished two goals. Although particulate matter was removed, small uniform-size spheres were dispersed throughout the film, a granular submicron ultra structure existed, and stress fractures were present from film drying. In order to minimize both voids and spheres, the thickness of the film casting was controlled to maximize coagulation rates, thus eliminating phase inversion holes while reducing the crystallite size. It was concluded that a film thickness of 1 mil or less and coagulation in pH-7 water would optimize the film's appearance.

Finally, while the high pressure batch filtration device resulted in film free of particulates >0.5 μm, it proved impractical for large-scale processing.

During the third year of the film processing program, we focused on the uniaxial, and particularly biaxial, extrusion of PBO polymers. Most of our efforts centered around the high intrinsic viscosity (40+) dope processed with the Berstorff twin screw extruder and the counter-rotating die, as described in previous annual reports. Utilizing the experience obtained in the first 2 years of the program we made modifications to the process steps to produce PBO film of improved optical quality and mechanical properties.

The work that we accomplished can be summarized as follows:

- We optimized the conditions for PBO degassing and homogenization.

- We instituted a number of processing improvements which we were better able to control the film orientation and uniformity while minimizing particulates and "football" inclusions.

- We systematically studied the effects of processing parameters on PBO film properties. The effect of processing variables such as draw ratio, mandrel speed, and throughput are summarized in Table 1.

Table 1. Effects of Processing Variables on PBO Film Properties

Variable	Effect
Post die draw	Used to control thickness. No significant change in mechanicals by using different annuli; gauge variations higher with larger annulus. Mechanicals best at a dry film thickness of 0.2 mil
Throughput	Effect on mechanicals not quantified, although thickness variation is reduced at lower rates
Die Mandrel Speed	Used with throughput to control the orientation. MD properties decrease with increasing Θ; ±22.5 deg film is most symmetrical and uniform in thickness

Characterization techniques included optical loss measurements, optical microscopy, tensile properties, and micrometer measurements on film thickness. Optical loss was improved to about 500 cm^{-1} corrected for an index of refraction of 1.6; this value, however, is still much greater than required for NLO materials. Thickness variations of less than about 8 percent were obtained after the processing modifications were made, while the asymmetry of tensile properties was approximately 10-15 percent. Machine direction tensile properties decreased with increasing angle of orientation, as expected. The properties tended to be optimal at a dry film thickness of 0.2 mil. Under these processing conditions, the bubble was hydrodynamically stable. Finally, the optical microscopy showed that we were able to obtain particulate free film with only a small number of inclusions (such as footballs) and voids. However, there seemed to always be orientation variations in the film as elucidated using crossed polarizer/analyzer.

The process modifications and improvements made during the third year are discussed in Section 2 of this report. The optical and mechanical properties of the PBO are described in Section 3.

2. THIRD-YEAR PROCESSING MODIFICATIONS AND IMPROVEMENTS

2.1 Acquisition of PBO Dope

During the final year of this program, PBO dope was acquired from DOW Chemical Company at various times. These batches were of differing nominal intrinsic viscosities (IVs) which are shown in Table 2. Although the measured IV did not vary much between the batches, the appearance and color did. Specifically, the nominal 17 IV PBO dope, even after degassing and homogenizing in the twin screw extruder, was difficult to process and "streaky" in appearance when extruded as film. These issues will be explored further in the PBO film characterization section.

2.2 PBO Dope Homogenization

As mentioned above, for PBZ polymers it was found to be necessary to degas, homogenize, and filter the dope prior to film extrusion. The processing conditions for the PBO polymer dope, however, had to be modified somewhat. While we also intended to process dope of lower percent solids in order to better homogenize the material, viscosity curves obtained from DOW indicated that actual processing viscosity (as opposed to IV, a measure of the molecular weight) actually decreased slightly with increasing solids concentration in the nematic range (9 percent to 14 percent solids). Those results further indicated that the viscosity was not significantly affected by temperature above 255°F and that degradation was not excessive up to 390°F. Like most nematic

Table 2. PBO Dope IV

DOW Nominal IV	FMI Measured IV	
	Before Degassing	After Degassing
17	19.6	15.0 (no filter) 21.5 (10 μm filter)
40	22.7	-
44	22.6	26.1 (400 mesh filter)
44 (2nd batch)	20.2	-

liquid crystalline polymers, the PBO dope was extremely shear sensitive. Thus, the distributive mixing was greatly enhanced at high screw speeds. The extruder run conditions are listed in Table 3.

The next section of the report will detail the processing modifications and improvements made during the third year of the program.

2.3 Process Modifications

In Table 4 the improvements made to the lyotropic film system this past year and their effects on the film characteristics are enumerated. While the first two items, degassing/homogenizing and fine filtering, were instituted earlier for the PBZ material, they were adapted for PBO in the final year of the program.

Table 3. PBO Extrusion Conditions

Degassing: Berstorff twin screw extruder
- Melt temperature: 350°F
- Screw speed: 250-300 RPM
- Metering pump: 45-56 RPM
- Vacuum: 28-29 in. Hg
- Extruder pressure: 1600-2000 psi

Film Runs: 3/4 in. Killion extruder with counter-rotating die
- Annulus gap: 0.014 in. or 0.052 in.
- Melt temperature: ≈ 300°F
- Mandrel speeds: 1-4 RPM, depending on orientation desired
- Metering pump: 30-60 RPM, depending on orientation
- Coagulation: 100°F water, deionized, deaerated and filtered
- Extruder pressure: 1000-1500 psi

Table 4. Recent Improvements to Lyotropic Film System

Improvement	Effect
Degassing/Homogenizing	Improvement mainly in the film clarity and homogeneity
Filtering	Using 5 or 10 μm filter during degassing improves the dope homogeneity with fewer particulates
Bifurcated die entry	Provides more uniform flow of dope through die; reduces runout
Controlled pressure to feed ram	More uniform flow to gear pump and pressure in extruder
Feed pot temperature controller/readout	Better flow to extruder
Improved N_2 flow meters	More sensitive bubble control
Smart system	Feedback control to all motors (mandrels, pumps, take-up)
Teflon sizing ring	Reduces bubble wander and controls diameter. Improves film uniformity
Water in take-up tank (and inside bubble)	Deaerated, filtered, deionized warm water reduces surface flaws

By employing a bifurcated die entry, feedback control system for the pumps, mandrels, and take-up (instead of using difficult to control potentiometers), improving the controls on the feedpot and flowmeters for blowing the bubble, and installing a Teflon sizing ring, the film uniformity was markedly improved. By uniformity, we are referring primarily to the circumferential thickness variations as well as longitudinal thickness and diameter variations. These variations directly affect the orientational distribution in the final film.

2.3.1 Teflon Sizing Ring

One of the most important of the above-mentioned modifications for controlling the axial and circumferential uniformity of the extruded film was the installation of the Teflon sizing ring. Starting with the November 1990 PBO film run, this ring was used to better control the bubble blowing process, as shown in Figure 6. The sizing ring was placed at the water line, where the bubble is already fully formed. To ensure constant diameter, the film bubble is blown against the wall of the Teflon ring.

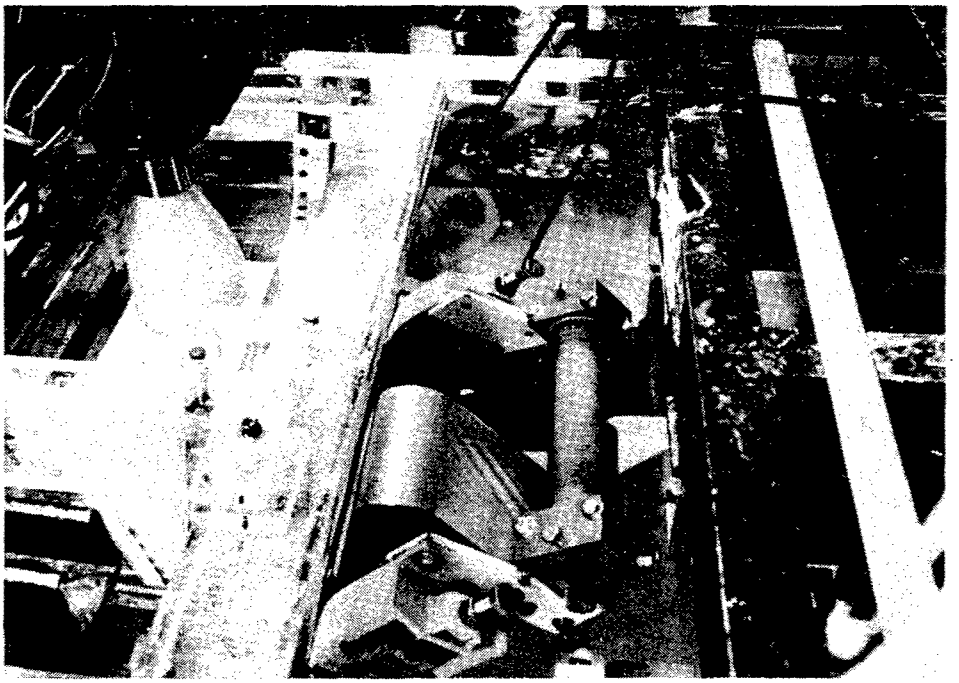


Figure 6. Lyotropic Die and Take-up System Showing Teflon Sizing Ring

An important effect of the Teflon sizing ring technique, discussed earlier, is that it has reduced the diameter variations of the final bubble size. Also, it contributed to a more stable film bubble during extrusion, which in turn has resulted in fewer film wrinkles. A reduction in diameter variation corresponds directly to a reduction in a final dry film axial thickness variation. The progress made with the sizing ring technique is shown in Figure 7, in which the standard deviation in thickness of tensile specimens is shown for various PBO film run dates, both before and after the installation of the Teflon ring. It can be seen that by this measure the film uniformity increased by about 25 percent for all but the 17 IV dope.

2.3.2 Coagulation Bath

The take-up system was modified extensively to provide for rapid coagulation of the extruded film as the PBZ hand-cast films had shown that this was desirable. Also, deaerated, deionized, filtered water was used in the coagulation bath and inside the blown bubble after the October 1990 film run. Furthermore, a heated bath of about 35°C has been employed to increase the rate of coagulation and consequently decrease crystallite size (and hence, scattering). The effects of these changes are most readily observed in the optical micrographs and optical loss measurements made on dried film, which will be discussed in the PBO film characterization section to follow.

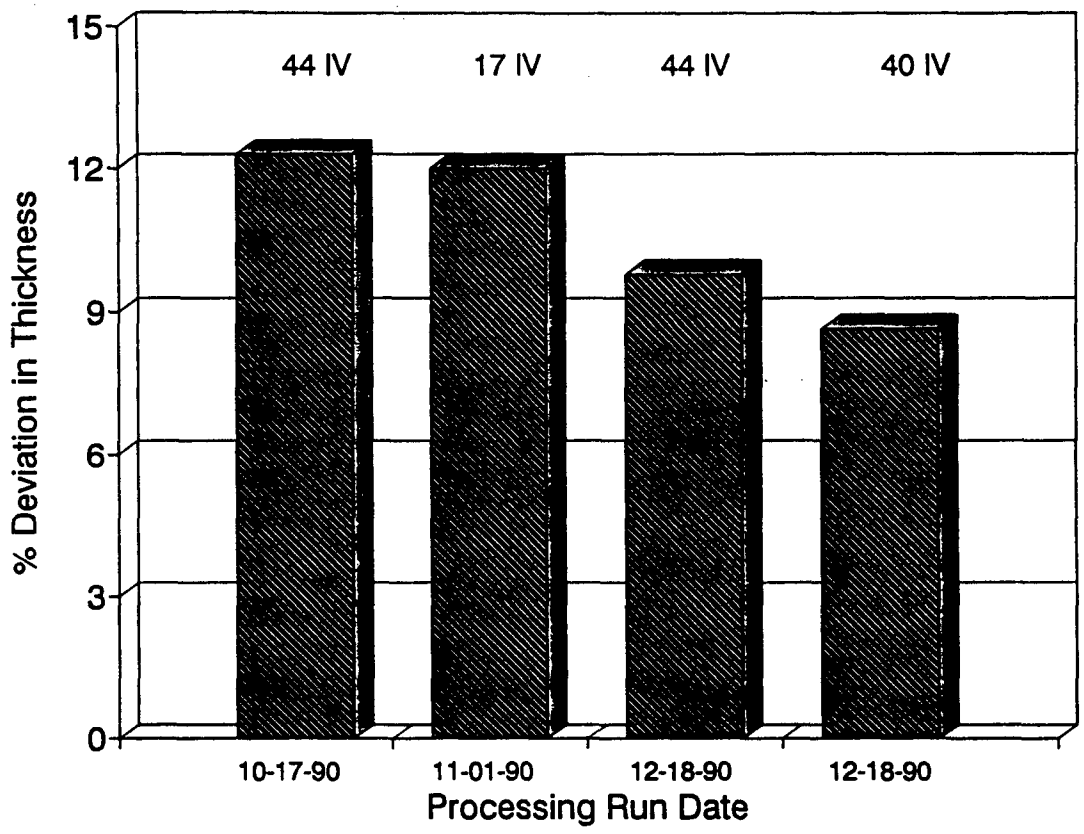


Figure 7. Thickness Variability of PBO Film

3. PBO FILM CHARACTERIZATION

As mentioned in Section 2, several methods were used to characterize the PBO film. The optical loss associated with light passing through the dried film is the single most important property. As mentioned in the summary, processing improvements have led to only minor decreases in alpha in the PBO film. Other techniques to characterize the film included optical microscopy, both in transmission and in reflectance, and tensile properties measured at different orientations with respect to the extrusion direction.

3.1 Optical Loss Measurements

Optical loss measurements have been performed on several PBO films which differed in orientation and thickness. The method employs a linearly polarized Helium-Neon laser and a Newport Research Corp. Silicon-Lithium Photodetector with a NRC 835 Optical Power Meter. The setup and equations used to calculate alpha have been detailed in previous reports.

The results of the measurements are presented according to run date in Figures 8 to 10. The average uncorrected value of alpha for 22.5 deg, 0.2-mil films was 818 cm^{-1}, but decreased as process modifications were made to a value of 484 cm^{-1} for the December 1990 run when corrected for an approximate index of refraction of 1.6, as seen in Figure 8. No specific trends were apparent with respect to film thickness or overall draw ratio (defined as the reduction in the cross-sectional area during draw down before coagulation). Some trend with biaxial orientation, $\pm\Theta$, however, could be noticed for the 0.1-mil film, with higher orientations giving lower losses, as seen in Figure 9. Finally, the highest (worst) values of alpha correspond to films extruded in November 1990, and thus originate from the dope batch with an IV designation of 17, as seen in Figure 10.

It should be reiterated, however, that even with corrected alpha values of 500 cm^{-1} for some PBO films is prohibitively high for NLO materials.

3.2 Optical Microscopy

Photomicrographs of film samples correlating to the five highest and five lowest values for alpha were visually analyzed for white light scattering (wavelength dependent: color variations in photomicrograph) and the presence of particulates and defects. The films with the five lowest

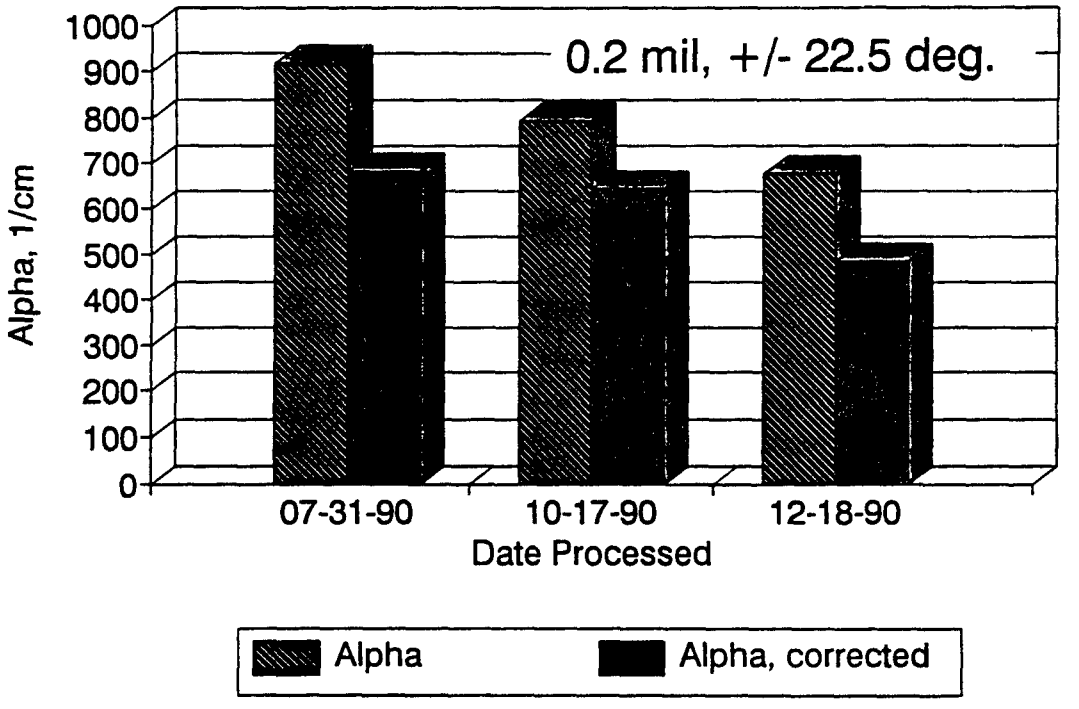


Figure 8. 44 IV PBO Film Optical Loss

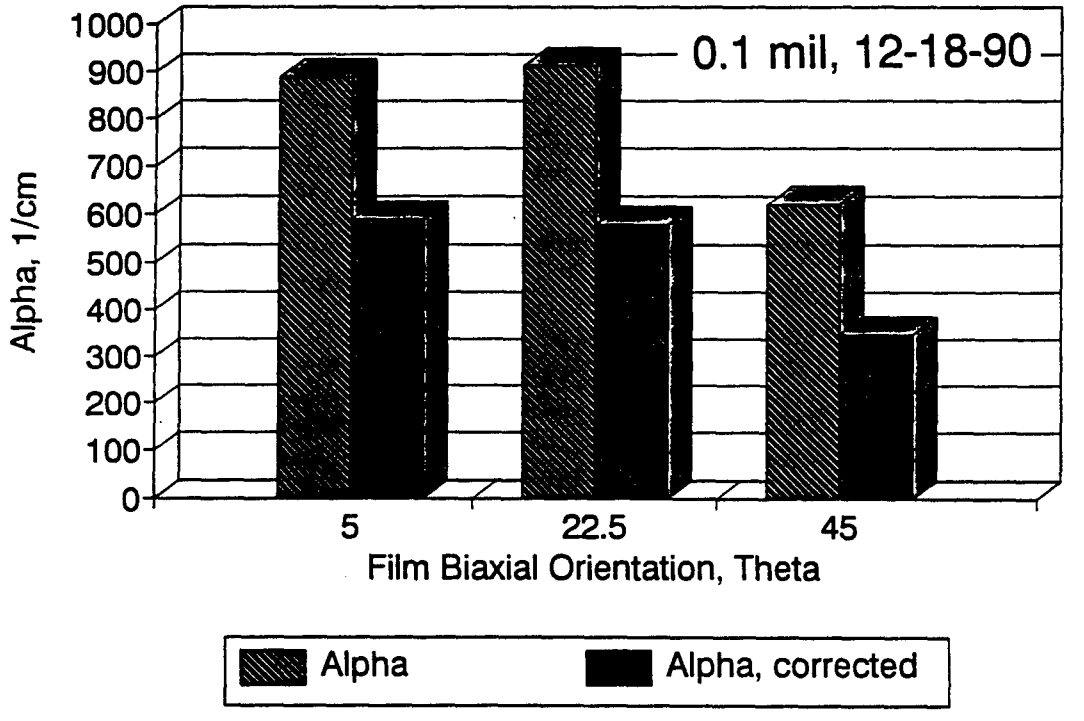


Figure 9. PBO Film Optical Loss as a Function of Biaxial Orientation

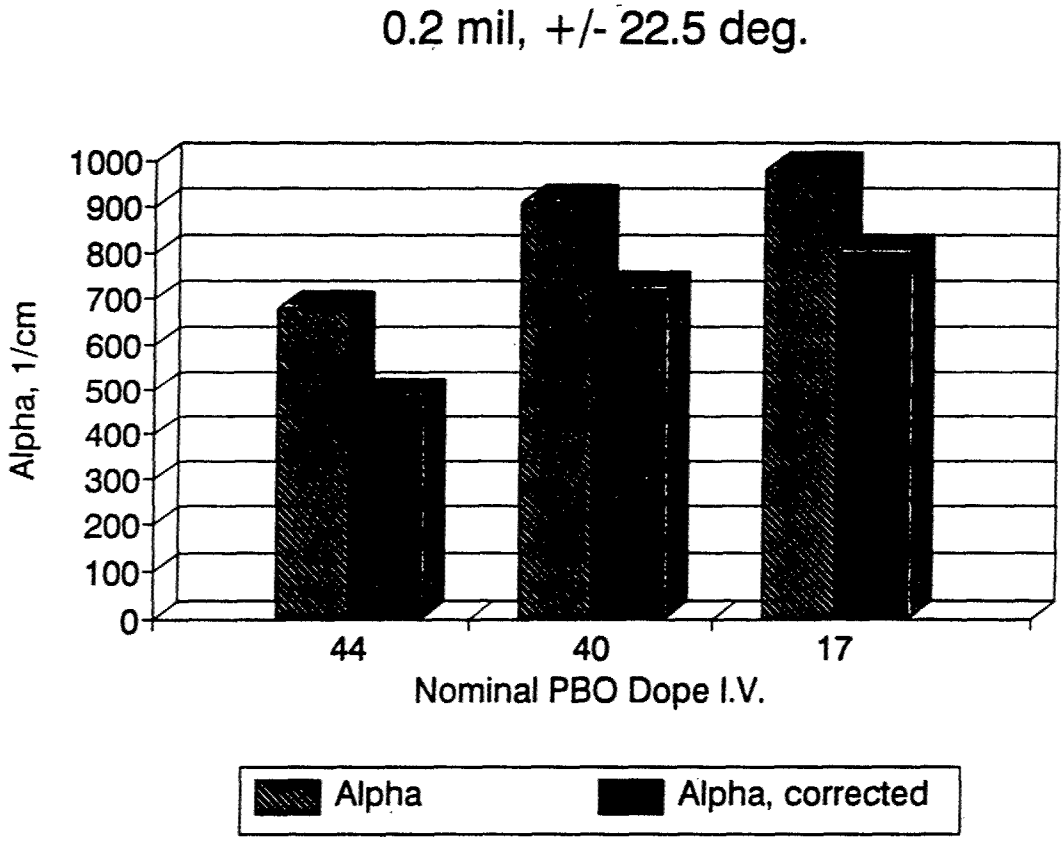
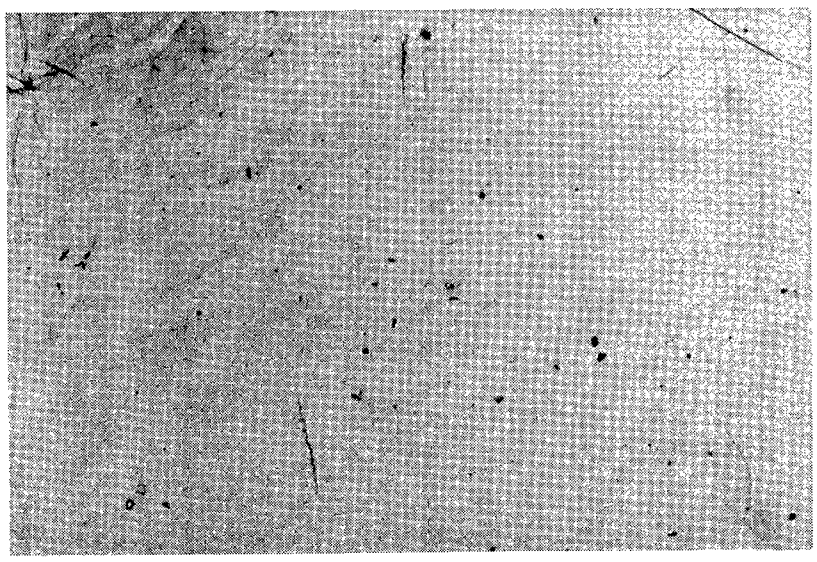


Figure 10. PBO Film Optical Loss from Different Batches

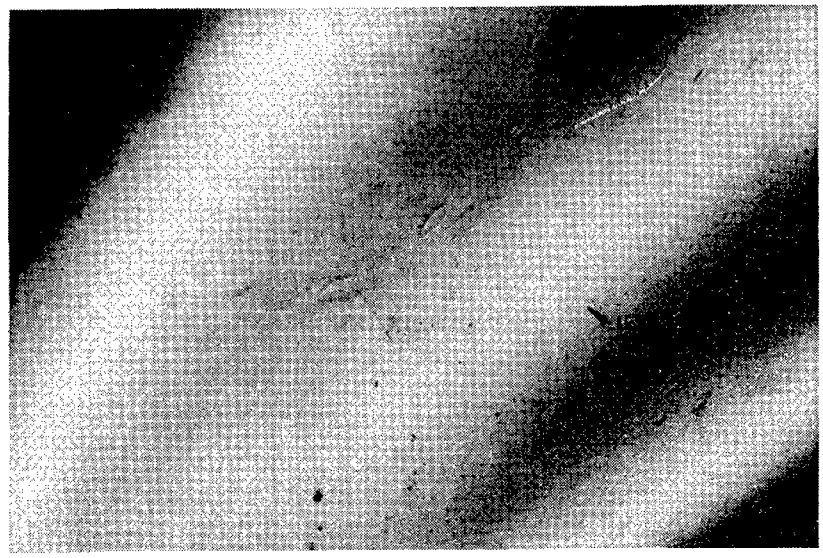
values generally exhibited a relatively low to moderate amount of scattering (color variation) and particulate/"football" density. Films with the five highest values of alpha, on the other hand, generally exhibited more optical scattering than the films with low alpha. These films possessed a relatively high density of "footballs" and what appeared to be tiny particles.

These trends are more clearly seen in Figures 11 and 12. In Figures 11a and 11b, a 0.1-mil, ±22.5-deg film is shown at 50x magnification both in transmission and reflectance; very few particulates are present. Significantly, the alpha value (n = 1.6) was only 514 cm^{-1} for this sample. In contrast, in Figure 11c is shown a micrograph of a ±22.5 deg film that was degassed without a fine filter, the surface of which is clearly strewn with particulate matter. For that run (November 1990) without a filter during degassing, the average corrected alpha was 956 cm^{-1}.

Some photomicrographs were also taken with crossed polarizer and analyzer to better elucidate the fibril orientation. The most noticeable difference detected with crossed polars was the effect of near-uniaxial orientation. In Figure 12 the difference between ±5 deg and ±22.5 deg biaxial film is



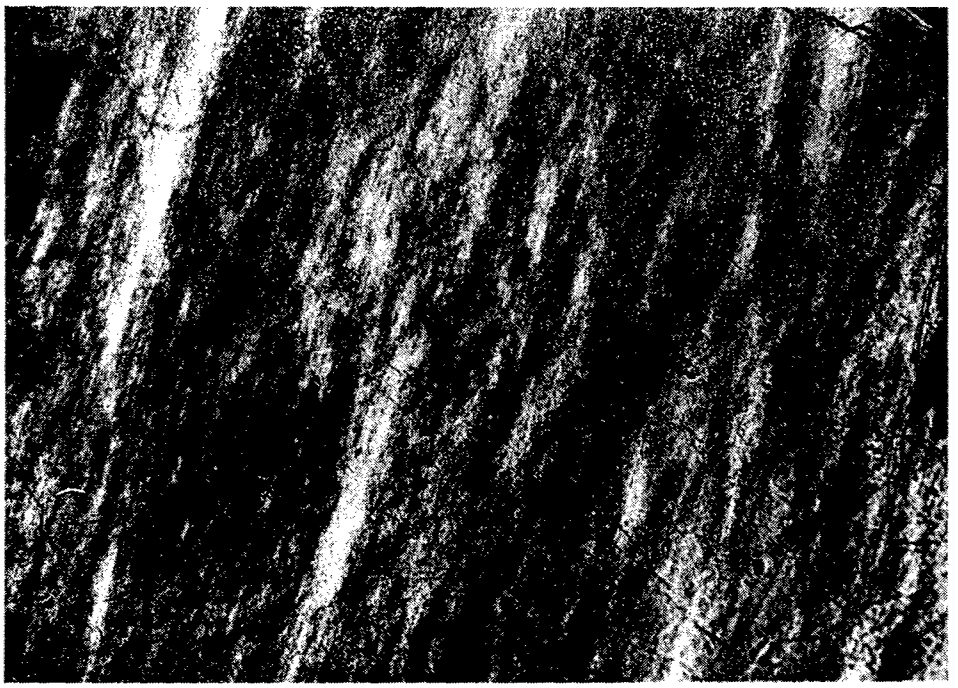
(a)



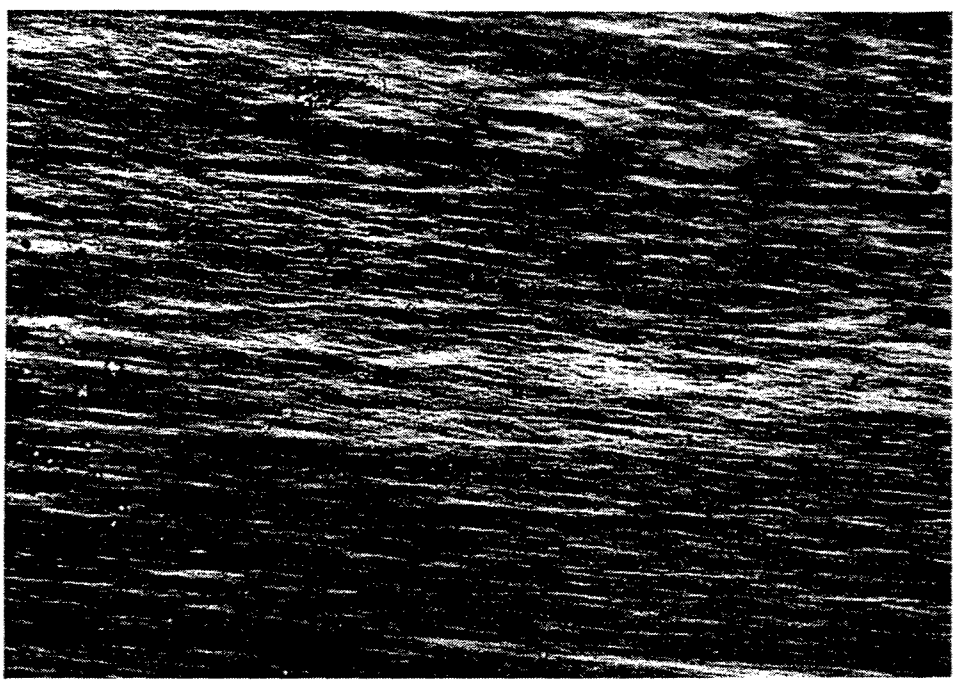
(b)

(c)

Figure 11. Optical Micrographs of PBO Film: a) In Transmission, Degassing with 10 μm Filter, b) In Reflectance, Degassing with 10 μm Filter, and c) In Reflectance, Degassing without a Fine Filter



(a)



(b)

Figure 12. Optical Micrographs Taken with Crossed Polars: a) ±22.5 deg Film, and b) ±5 deg Film

readily apparent. The near-uniaxial film (Figure 12a) shows orientation domains that are much narrower, whereas the 22.5 deg (Figure 12b) and 45 deg film (not shown), the domains appear to be more spread out.

3.3 Mechanical Properties

The measurement of mechanical properties, in addition to allowing comparison of absolute values, can also give information on the orientation angle and orientational symmetry of the film. Polar plots, in which properties are measured at varying angles around the film, can yield information on the orientation. From the polar plots (or without even doing a complete plot), one can abstract further information. The "+ fiber direction / - fiber direction" ratio for either strength or modulus provides a measure of the symmetry of orientation, with unity being the ideal value and deviations from unity representing increasing asymmetry in orientation. The ratio of machine direction to transverse direction properties (MD/TD) gives an idea of the degree of anisotropy in the film. For example, completely uniaxial film may have MD/TD ratios as great as 100, ±5 deg film may have ratios of 20 to 30, ±22.5 deg film typically shows an anisotropy ratio of 3, and ±45 deg film should of course have equal machine and transverse properties. The following paragraphs correlate the mechanical behavior with processing variables, PBO dope batch, and system modifications made during the past year.

3.3.1 Effect of Processing Improvements and PBO Dope Batch

As with the optical loss measurements and optical microscopy results, the mechanical properties varied with PBO dope batch and with the improvements made to the processing system during the third year. In Figure 13 the machine direction modulus and strength are plotted as function of processing run date for the 44 IV, 0.2 mil ±22.5 deg film. While the strength remained in the 125 to 150 kpsi range, the modulus, which better reflects the perfection in orientational order of the PBO molecules, increased 50 percent from 6 to 9 Mpsi. The orientational symmetry, given by (+FD)/(-FD), also decreased when the processing modifications to better control the film bubble were made, as shown in Figure 14. The difference between this ratio and unity is plotted on the bar graph, and shows values about 0.15 for the December 1990 run. Notably, the nominal 17 IV PBO film exhibited much higher asymmetry in orientation, reflecting the greater instability in the bubble because of the nonuniformity of the film. The MD/TD ratio is plotted in Figure 15 for different batches and run dates, and shows no clear trend with either parameter. Values of this parameter for the ±22.5 deg film of 2.5 to 4 are typical. The notable exception is the 44 IV dope

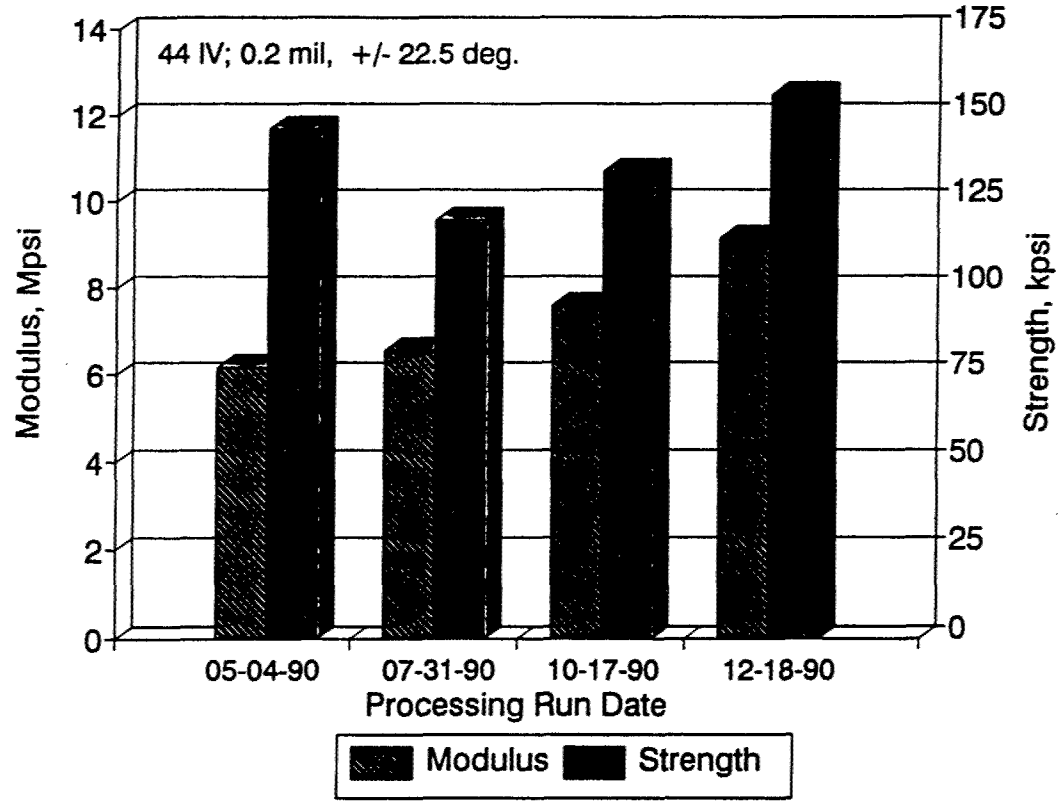


Figure 13. MD Tensile Properties of PBO Film

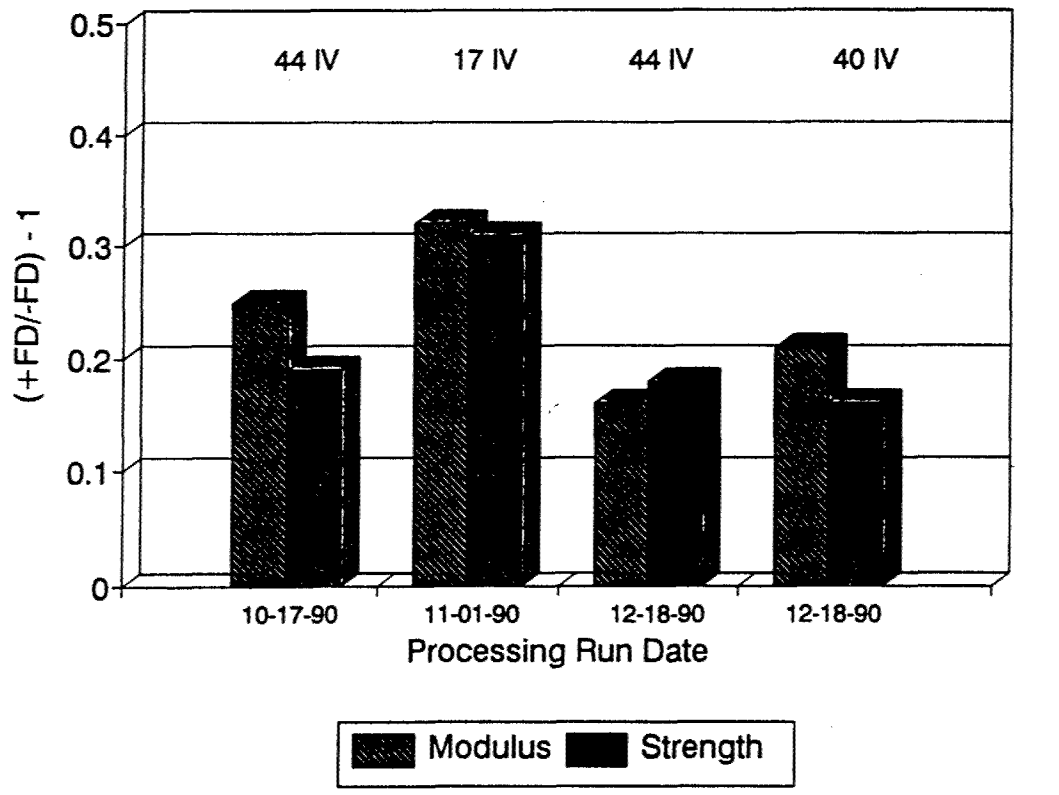


Figure 14. Orientational Symmetry of PBO Film

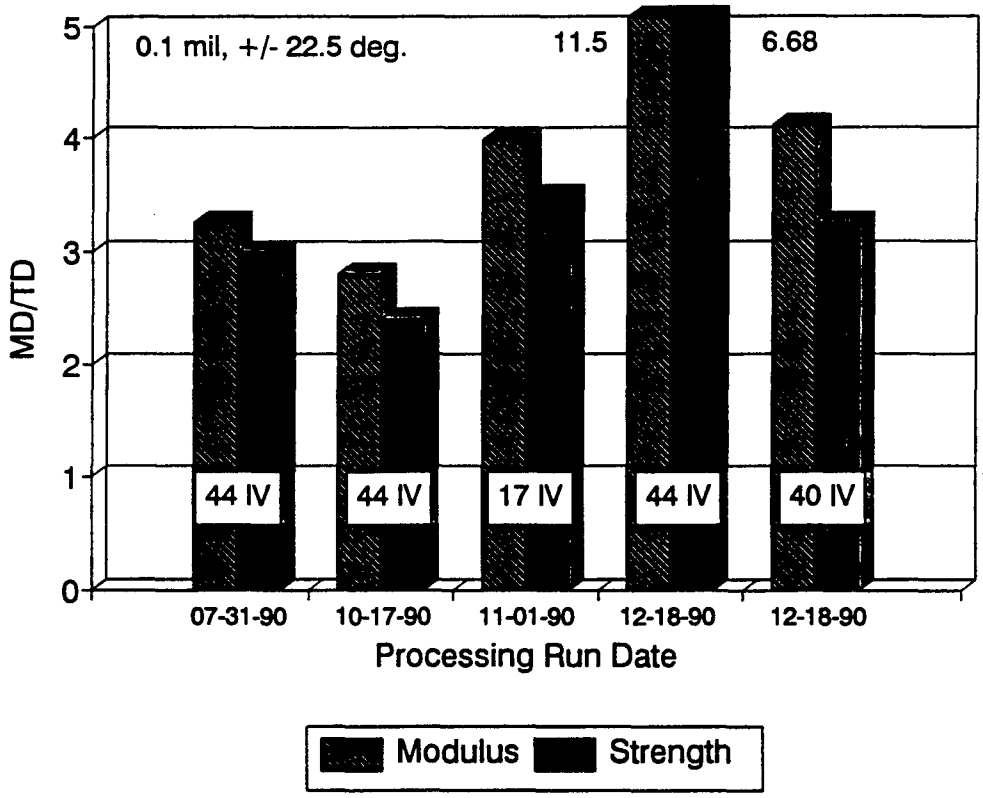


Figure 15. MD/TD Property Ratio of PBO Film

for the December 1990 run, in which transverse properties were significantly lower than expected, causing the MD/TD ratio to balloon. This finding is difficult to account for, but is also observed in the polar plots, shown for modulus values in Figures 16 and 17. Figure 16 shows the data for the film from December 1990, and represents a MD/TD modulus ratio of 8.9. Figure 17 represents ±22.5 deg film from the 40 IV dope of the December 1990 run with the MD/TD modulus ratio a more typical 4.6.

Variations with PBO dope batch are also observed in the magnitudes of the tensile properties, shown in Figures 18 and 19. For both 0.1 and 0.2 mil ±22.5 deg film the properties are best with the 44 IV PBO, and worst with the 17 IV PBO, as expected. Since all these data were taken after the latest processing modifications, they represent a fair comparison.

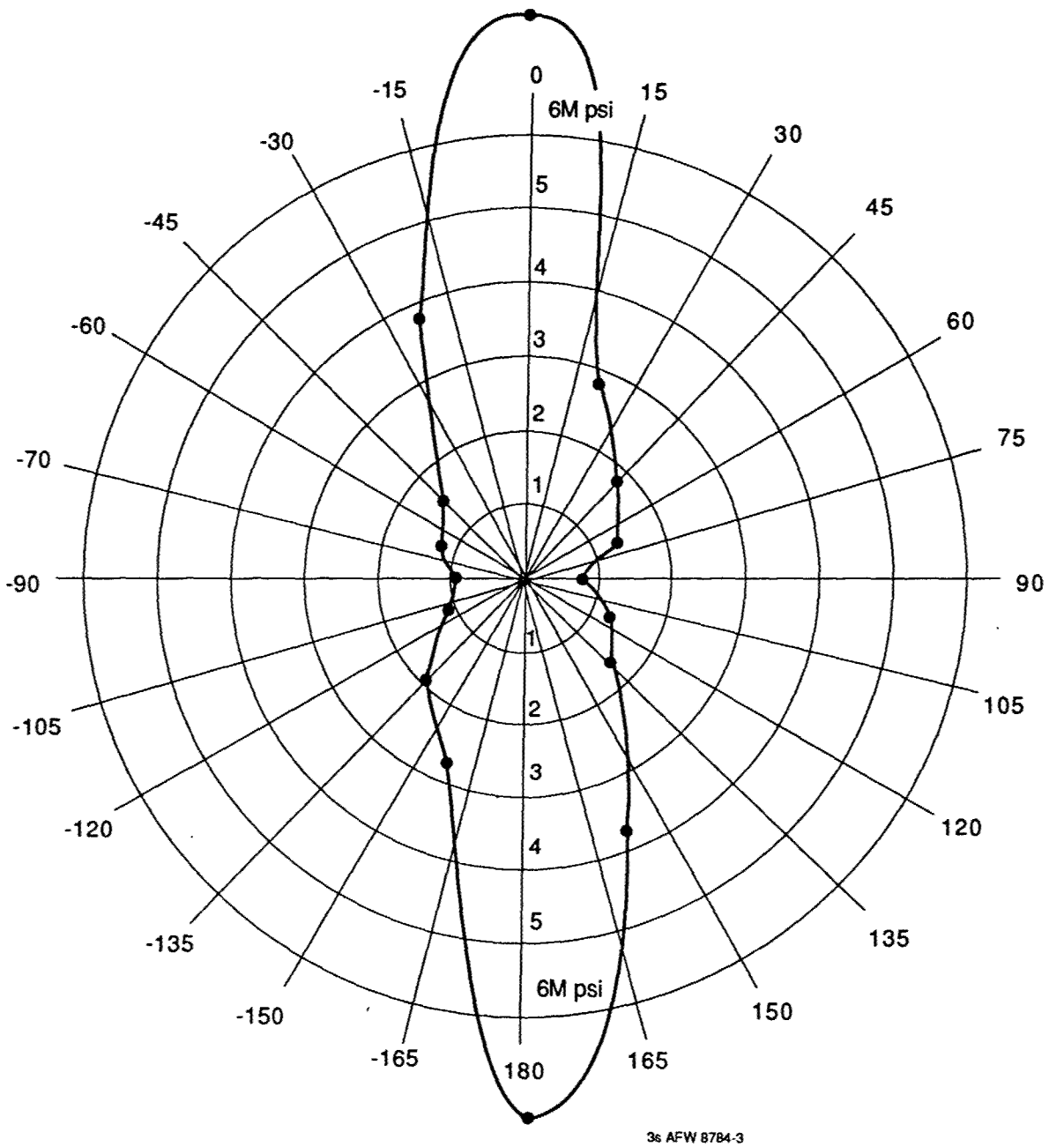


Figure 16. Polar Plot of Modulus: 44 IV, 0.2 mil ±22.5 deg Film

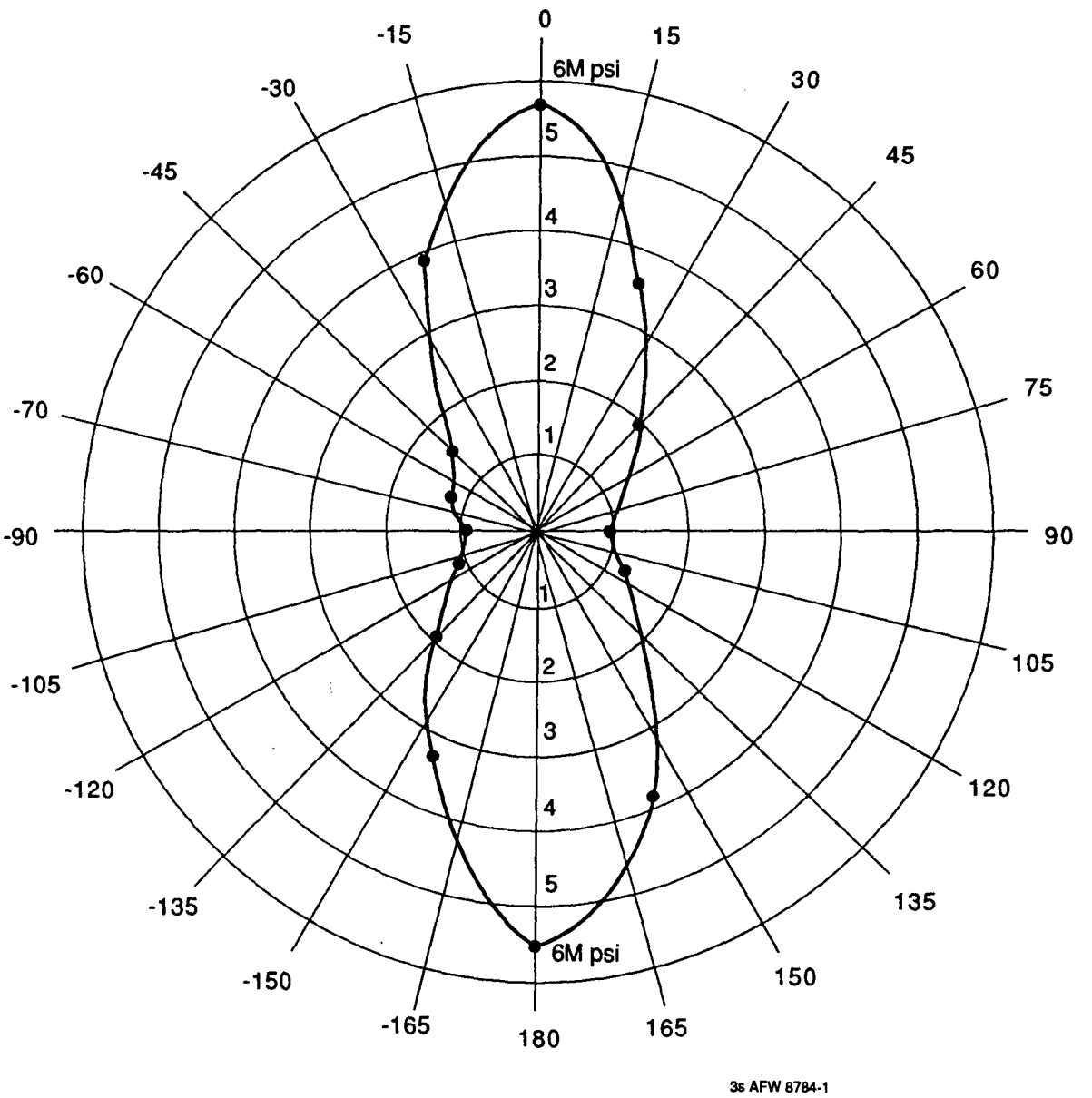


Figure 17. Polar Plot of Modulus: 40 IV, 0.2 mil ±22.5 deg Film

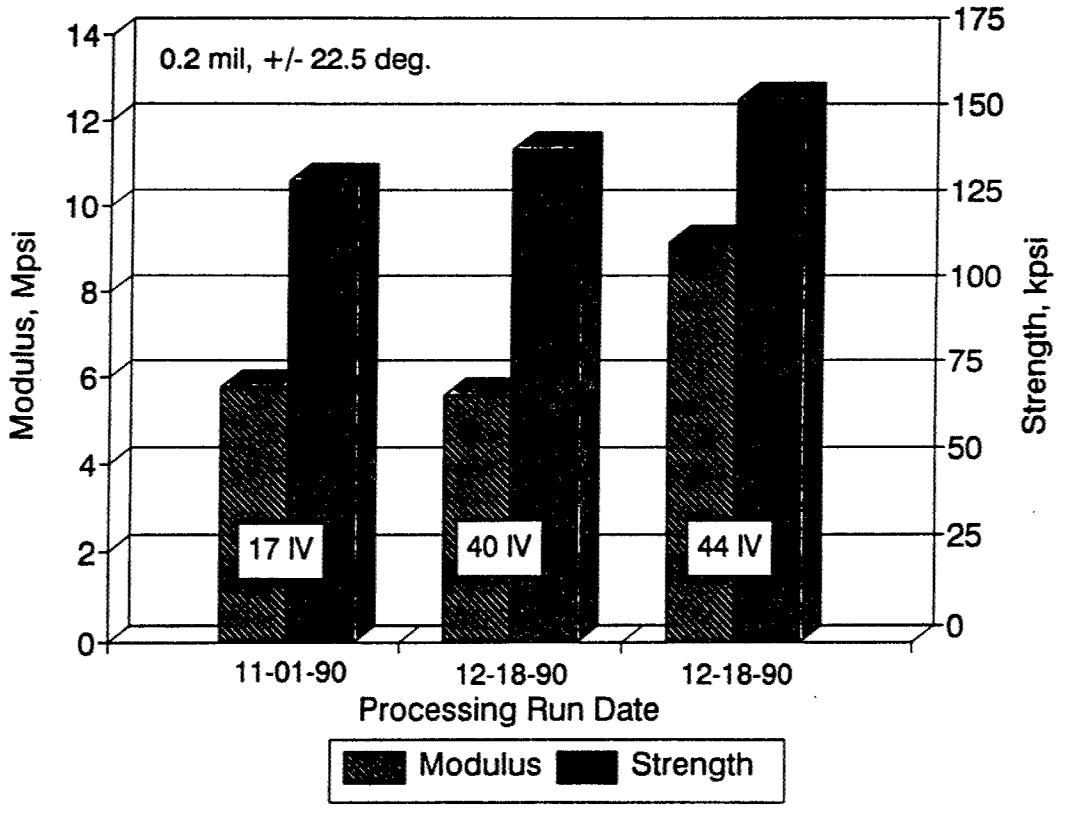


Figure 18. MD Tensile Properties of PBO Film: 0.1 mil ±22.5 deg

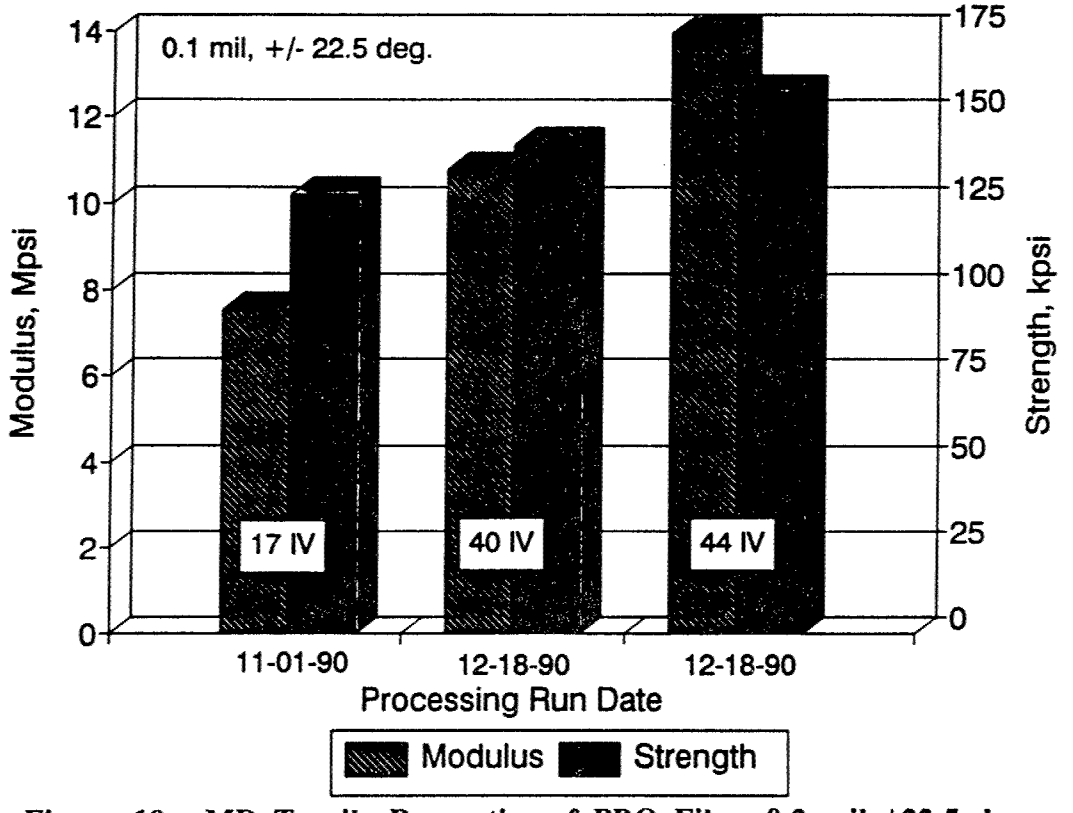


Figure 19. MD Tensile Properties of PBO Film: 0.2 mil ±22.5 deg

3.3.2 Effect of Biaxial Orientation

Plots of the ratios MD/TD and +FD/-FD modulus versus biaxial orientation are shown in Figure 20 for 0.2-mil film extruded from 44 IV dope. We can see that the optimum value (unity) for +FD/-FD modulus occurs at approximately 22.5 deg. However, the +FD/-FD ratios increased from 1 at ±22.5 deg to 1.4 at ±45 deg. This result characterizes a biaxial asymmetry which generally increases for the extremes in biaxial orientation angle, reflecting less stability in the blown bubble. The data for MD/TD modulus and strength ratios, also shown in Figure 18, had a value of approximately 2.25 at ±22.5 deg orientation. The MD/TD values decreased to the expected value of unity at ±45°.

In Figure 21 we see the expected trends in machine direction modulus and tensile strength with increasing biaxial orientation angle, Θ. A monotonic decrease in machine direction properties with increasing angle of orientation is observed. Polar plots can better show the effect of film orientation angle. In Figure 22, a polar plot of the tensile strength of the balanced biaxial (±45 deg) film exhibits a broad, near circular geometry as expected (MD/TD = 1.4). This result is contrasted to the ±22.5 deg film tensile strength polar plot which has distinctly anisotropic characteristics (MD/TD = 5.7), shown in Figure 23..

3.3.3 Effect of Thickness

Film thicknesses (coagulated) obtained from the 14 mil die ranged from 0.05 mil to 0.5 mil. However, the measured values of thickness for the 0.05 mil films indicated actual thicknesses of 40 percent to 120 percent greater than calculated. Further, low draw ratios for films of greater than 0.5 mil thickness caused irregular bubble gyrations during the blowing process. Thus, the "standard" film thicknesses of 0.1 mil to 0.5 mil arose from drawdown limitations for the 14 mil annulus die: hydrodynamically stable bubbles could not be obtained outside of this regime. Although some work was also conducted with the 0.052 mil die, the high "runout" precluded obtaining quality films, and in any case the drawdown required for suitably thin NLO films frequently resulted in bubble instabilities.

The maximum modulus for ±22.5 deg film, approximately 7.7 Mpsi, occurred at a 0.2 mil dry film thickness, as seen in Figure 24. However, the range of mean values is contained within the standard deviation bars of the endpoints of the plot. Thus, although an intermediate maximum occurred at 0.2 mil, its significance is limited.

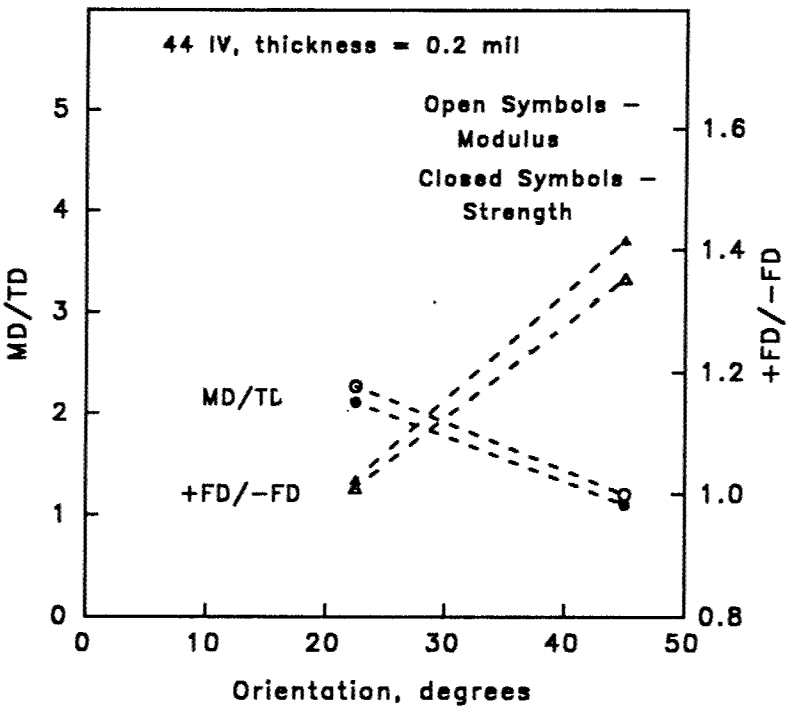


Figure 20. PBO Film Orientational Symmetry at Different Biaxial Orientations

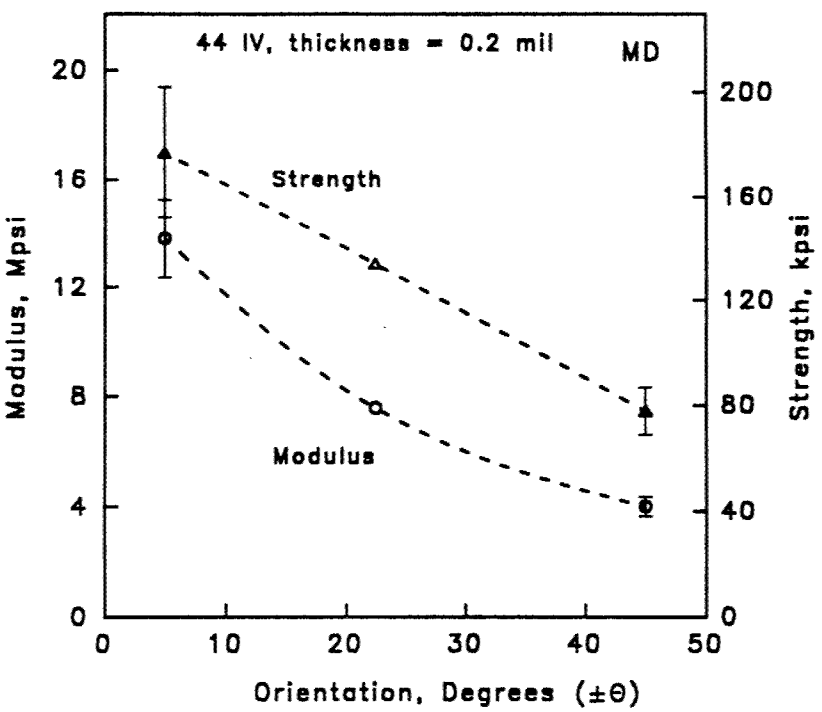


Figure 21. PBO Film Properties at Different Biaxial Orientations

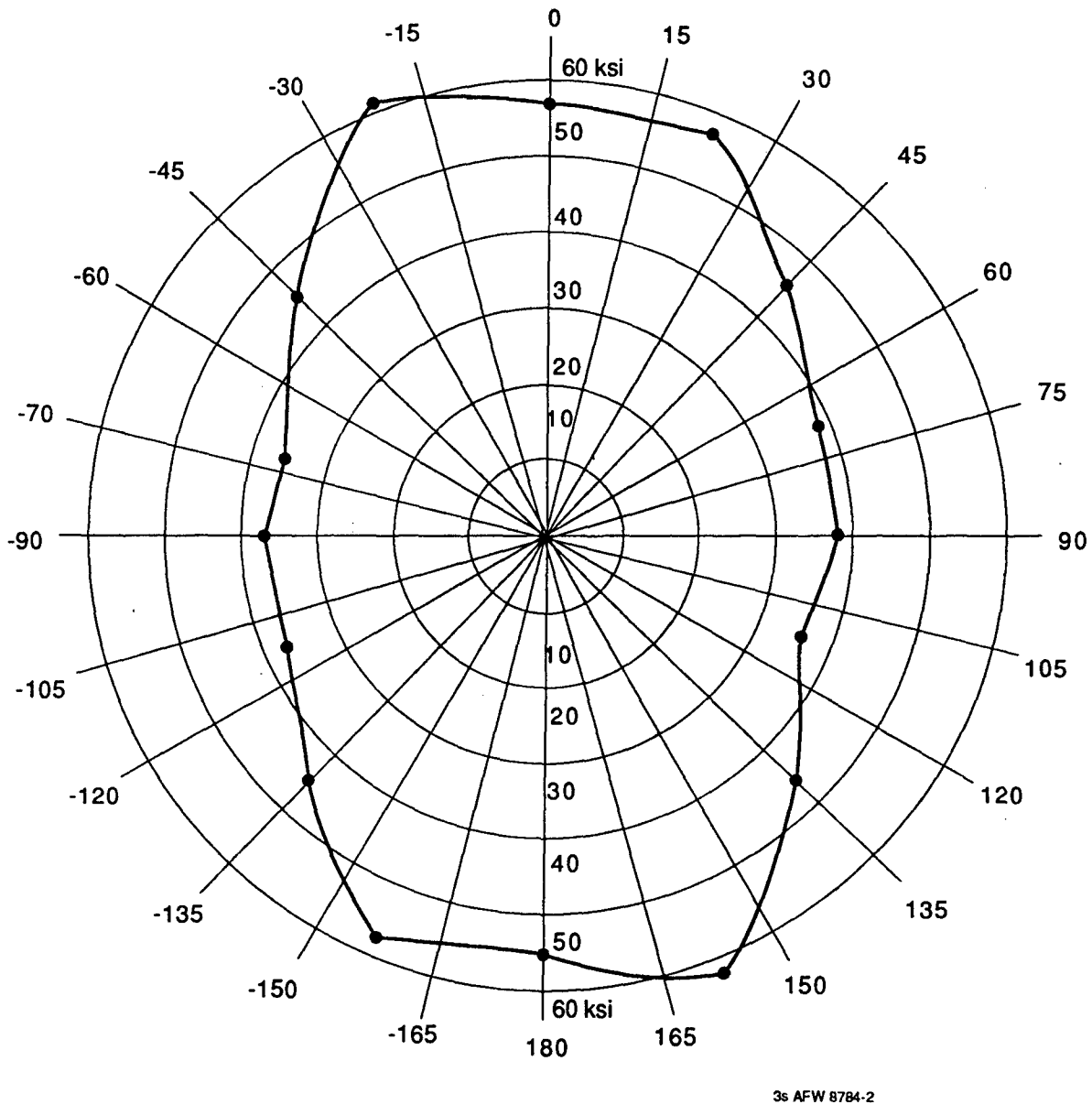


Figure 22. Polar Plot of Tensile Strength of 44 IV ±45 deg PBO Film

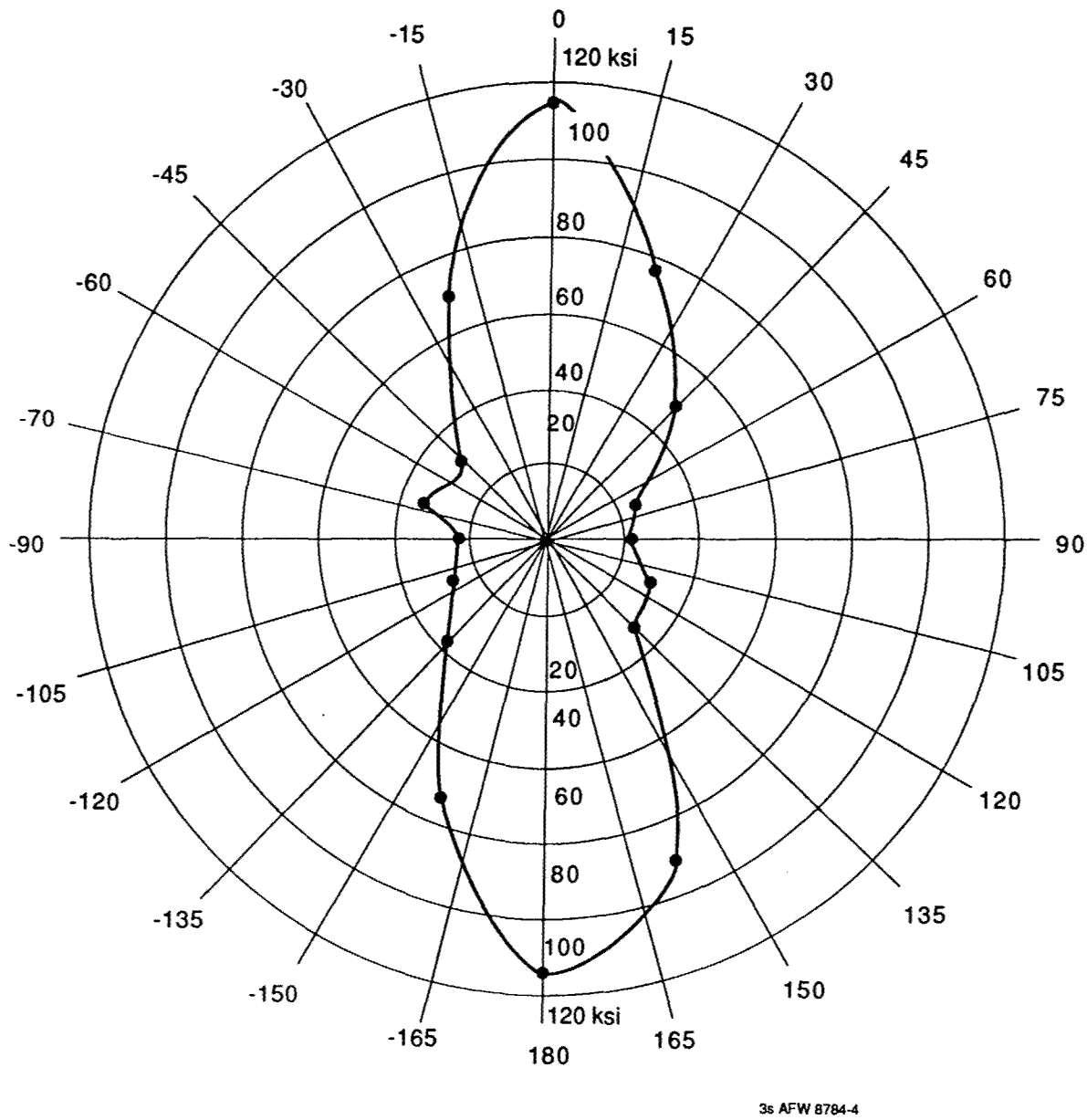


Figure 23. Polar Plot of Tensile Strength of 40 IV ±22.5 deg PBO Film

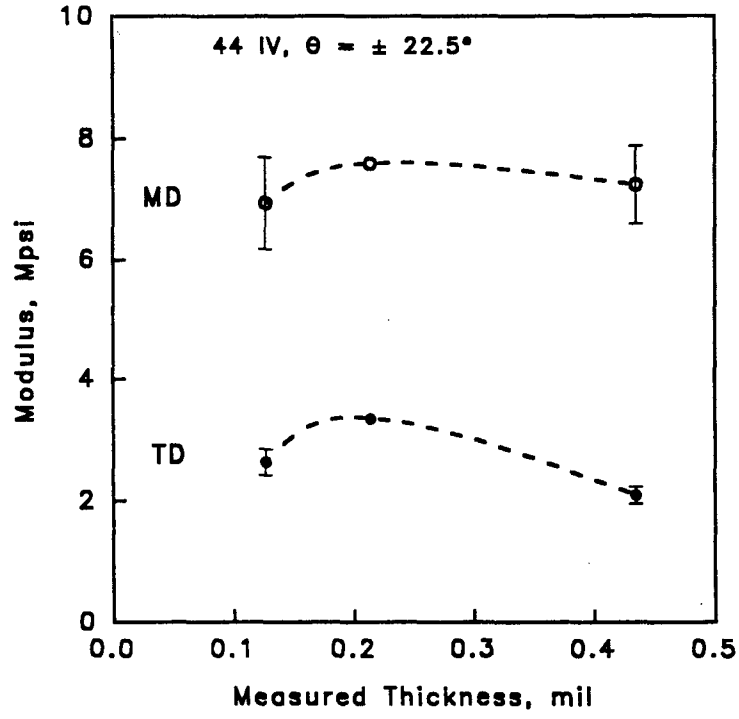


Figure 24. PBO Film Modulus at Different Film Thicknesses

With respect to transverse direction, the results were much more significant due to the generally smaller standard deviations. Again, the intermediate maximum modulus occurred at a thickness of approximately 0.2 mil. In the transverse direction the maximum is approximately 10 to 20 percent greater than the "mean + standard deviation" of the next lowest data point. Thus, the marginally optimum extrusion thickness for the PBO film in terms of mechanical properties appears to be 0.2 mil (coagulated).

The tensile strength measurements, plotted in Figure 25, display the same trends as the modulus, except that the machine direction trend is somewhat more significant. This finding once again indicates that the 0.2-mil film is the optimum thickness with respect to strength and modulus.

The biaxial fibril orientation appears to increase monotonically with thickness, according to the plots in Figure 26. In this figure, data are plotted for film with a nominal orientation angle of ±22.5 deg (IV of 44). The MD/TD ratio for modulus decreased uniformly with increasing measured thickness: from approximately 5.5 at 0.1-mil to 2.5 at 0.45-mil. Based on past experience, for ±22.5 deg film we expect a MD/TD ratio of approximately 3, as mentioned previously. For value greater than 3, the fibril orientation probably tends towards the machine

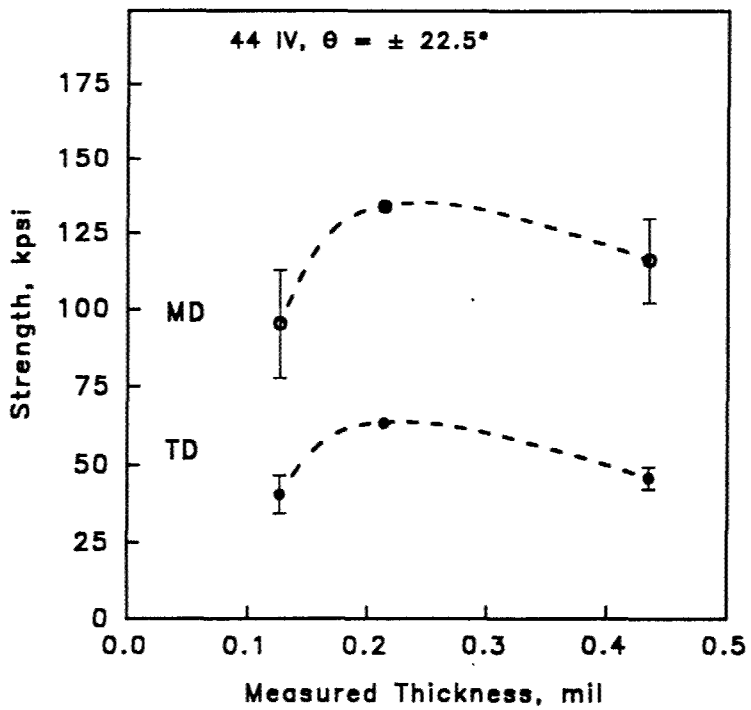


Figure 25. PBO Film Strength at Different Film Thicknesses

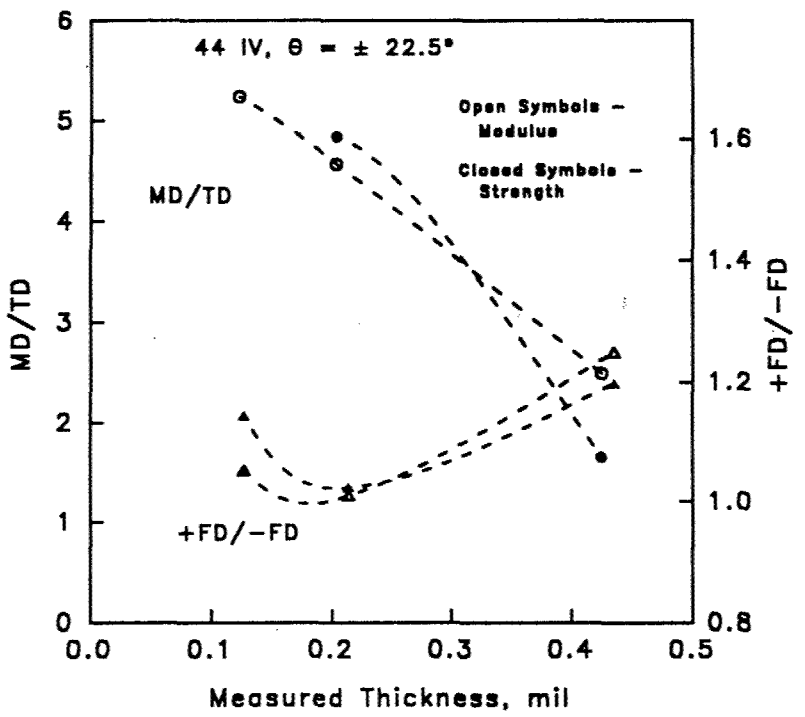


Figure 26. PBO Film Orientational Symmetry at Different Film Thicknesses

direction (MD/TD for ±5 deg film is approximately 30), while for values less than 3 the orientation tends towards the transverse direction. For the film represented in Figure 26, the MD/TD ratio for modulus has a value of 3 at approximately 0.4-mil. Also, the lowest value of +FD/-FD (near unity) for both strength and modulus corresponds to a thickness of approximately 0.2-mil, with increasing fibril asymmetry for the 0.1 mil and 0.45-mil films. Once again, in terms of orientational symmetry, the 0.2-mil film appears best.

4. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

During the third year of the film processing program, we focused on the uniaxial, and particularly biaxial, extrusion of PBO polymers. Most of our efforts centered around the high intrinsic viscosity (40+) dope processed with the Berstorff twin screw extruder and the counter-rotating die, as described in previous annual reports. Utilizing the experience obtained in the first two years of the program we made modifications to the process steps to produce PBO film of improved optical quality and mechanical properties.

The work that we accomplished can be summarized as follows:

- We optimized the conditions for PBO degassing and homogenization.
- We instituted a number of processing improvements which we were better able to control the film orientation and uniformity while minimizing particulates and "football" inclusions.
- We systematically studied the effects of processing parameters on PBO film properties. The effect of processing variables such as draw ratio, mandrel speed, and throughput, were summarized in Table 1.

Characterization techniques included optical loss measurements, optical microscopy, tensile properties, and micrometer measurements on film thickness. Optical loss was improved to about 500 cm^{-1} corrected for an index of refraction of 1.6; this value, however, is still much greater than required for NLO materials. Thickness variations of less than about 8 percent were obtained after the processing modifications were made, while the asymmetry of tensile properties was approximately 10-15 percent. Machine direction tensile properties decreased with increasing angle of orientation, as expected. The properties tended to be optimal at a dry film thickness of 0.2 mil. Under these processing conditions the bubble was hydrodynamically stable. Finally, the optical microscopy showed that we were able to obtain particulate free film with only a small number of inclusions (such as footballs) and voids. However, there seemed to always be orientation variations in the film as elucidated using crossed polarizer/analyzer.

Future Work

During the course of their three-year effort, great improvements have been made in processing controlled orientation films of lyotropic liquid crystalline polymer films. In order to produce large quantities of film, the process modifications still need to be made. These include bubble diameter control, continuous take-up, washing and drying. Additionally, with the development of Foster-Miller's orientation sensor system and software/hardware control, "expert" process control is ready to be implemented.

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